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Application Date: 2003 04 30

Application Number: 03 1 14399.7

Application Type: Invention

Title: Automobile Exhaust Catalytic Converter Devices

Applicant: BYD LTD.

Inventors: Chuanfu Wang, Junqing Dong, Chunbo Li, Yi Liu

People's Republic of China  
Commissioner of the State Intellectual  
Property Office (signed) Wang Jingchuan  
January 5, 2004

# 证 明

本证明之附件是向本局提交的下列专利申请副本

申 请 日： 2003 04 30

申 请 号： 03 1 14399.7

申 请 类 别： 发明

发明创造名称： 汽车尾气催化转化器

申 请 人： 比亚迪股份有限公司

发明人或设计人： 李春波； 刘毅； 王传福； 董俊卿



中华人民共和国  
国家知识产权局局长

王 景 川

2004 年 1 月 5 日

## 权 利 要 求 书

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1、一种汽车尾气催化转化器，包括壳体、减振层、金属载体及催化剂涂层，其特征在于：所述的金属载体为发泡金属材料，且发泡金属的发泡孔径为 50~1200 微米，孔隙率为 80~98%。

2、如权利要求 1 所述的汽车尾气催化转化器，其特征在于：所述的发泡金属材料，其组分表示为 AB，则：

A 组分为镍 Ni，其含量占发泡金属材料的 60~100wt %；

B 组分包括铬 Cr、铝 Al、铁 Fe、钴 Co、钼 Mo、锌 Zn、锆 Zr、钒 V、钛 Ti、铈 Ce、镧 La、铀 Nu 中的一种或几种，其含量占发泡金属材料的 0~40wt %。

3、如权利要求 1 或 2 所述的汽车尾气催化转化器，其特征在于：所述的发泡金属材料的发泡孔径为 400~800 微米，孔隙率为 95~98%。

4、如权利要求 1 所述的汽车尾气催化转化器，其特征在于：所述的催化剂涂层，其组分包括金属元素、稀土金属及少量贵金属，其中金属元素包括钙 Ca、钡 Ba、镁 Mg、锆 Zr、锌 Zn、铝 Al 中的一种或几种；稀土金属包括铈 Ce、镧 La、镨 Pr、铀 Nu 中的一种或几种；贵金属包括钨 Pb、铂 Pt、铑 Rh、钌 Ru 中的一种或几种。

5、如权利要求 4 所述的汽车尾气催化转化器，其特征在于：所述的催化剂涂层，其组分中还可加入  $\gamma$ -氧化铝、氧化锆、氧化铈中的一种或几种。

6、如权利要求 1 所述的汽车尾气催化转化器，其特征在于：所述的发泡金属材料是通过电镀方法制备的。

7、如权利要求 1 所述的汽车尾气催化转化器，其特征在于：所述的发泡金属材料的发泡孔壁表面形成有致密氧化层。

8、如权利要求 7 所述的汽车尾气催化转化器，其特征在于：所述的发泡金属材料发泡孔壁表面的氧化层是通过高温氧化或电化学阳极氧化或有机酸热腐蚀形成的。

# 说明书

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## 汽车尾气催化转化器

### 【技术领域】

本发明涉及一种汽车尾气催化转化器，具体地说涉及其催化剂载体。

### 【背景技术】

在汽车尾气净化系统中，催化剂是催化转换器的关键部件，其载体材料为陶瓷和金属两类。与金属载体相比，目前通用的蜂窝陶瓷载体存在着温度较低（1400℃软化）、元件壁较厚、预热慢、排气阻力较大等缺点。因此，各国都在进行金属载体的开发。金属载体壁厚仅为陶瓷载体的 1/4，因而可降低排气阻力。并使催化剂载体小型化成为可能；金属载体的热容量小，其预热性能好，有利于电预热催化剂实现 HC 的零排放措施的实施，另外还有温度适应性好等优点。

而目前汽车尾气催化转化器中催化剂的金属载体以金属波纹网组合成的各种结构为主，其耐热冲击和机械冲击性能较低，特别是高温时抗氧化能力不足，影响了汽车尾气催化转化器使用寿命。另外，这种波纹网状的金属载体，其比表面积有限，吸附催化剂活性组分能力不足，限制了汽车尾气催化转化器净化效率的进一步提高。

### 【发明内容】

本发明的目的是提供一种耐热冲击和机械冲击，净化效率高，使用寿命长的汽车尾气催化转化器。

本发明的目的是通过下述技术方案实现的：

一种汽车尾气催化转化器，包括壳体、减振层、金属载体及催化剂涂层，其中所述金属载体为发泡金属材料，且发泡金属的发泡孔径为 50~1200 微米，孔隙率为 80~98%。其中发泡孔径为平均孔径，即：以一定长度除以该长度内连续的径向相连的发泡孔数；孔隙率为材料中孔隙体积与材料在自然状态下的体积之比的百分率。

进一步地所述的发泡金属材料，其组分可表示为 AB，A 组分为镍 Ni，其含量占发泡金属材料的 60~100wt%；B 组分包括铬 Cr、铝 Al、铁 Fe、钴 Co、钼 Mo、锌 Zn、锆 Zr、钒 V、钛 Ti、铈 Ce、镧 La、钕 Nu 中的一种或几种，其含量占发泡金属材料的 0~40wt%。

再进一步地所述的发泡金属材料的发泡孔径为 400~800 微米，孔隙率为 95~98%。

所述的催化剂涂层组分包括金属元素、稀土金属及少量贵金属，其中金属元素包括钙 Ca、钡 Ba、镁 Mg、锆 Zr、锌 Zn、铝 Al 中的一种或几种；稀土金属包括铈 Ce、镧 La、镨 Pr、钕 Nu 中的一种或几种；贵金属包括钨 Pb、铂 Pt、铑 Rh、钌 Ru 中的一种或几种。

所述催化剂涂层组分中还可加入  $\gamma$ -氧化铝、氧化锆、氧化铈中的一种或几种。

所述的发泡金属材料是通过电镀方法制备的。

所述的发泡金属材料的发泡孔壁表面形成有致密氧化层。

本发明汽车尾气催化转化器的优点在于：耐热冲击及机械冲击，比表面积大，净化效率高，载体与催化剂涂层结合力强，使用寿命长。

下面参照附图结合实例对本发明作进一步的说明。

#### 【附图说明】

图 1 为本发明汽车尾气催化转化器剖面结构示意图。

图 2 为本发明汽车尾气催化转化器载体材料发泡孔放大结构图。

图 3 为本发明汽车尾气催化转化器实施例中载体发泡金属孔径与转化率特性曲线图。

#### 【具体实施方式】

请参考图 1，本发明提供的汽车尾气催化转化器，包括壳体 1、减振层 2、金属载体 3 及涂覆于载体上的催化剂涂层 4，其中所述金属载体 3 的材料为发泡金属材料，且发泡金属的发泡孔径为 50~1200 微米（为平均孔径），孔隙率为 80~98%。

图 2 为本发明汽车尾气催化转化器发泡金属载体材料的发泡孔放大结构图（用 JEOL 公司的 JSM—5610 测试），图中可清楚看到发泡金属具有三维网状结构，骨架彼此相连，所有孔隙相通，具有很高的孔

隙率和较高的机械强度。在本发明中，将其用于汽车尾气催化转化器载体，优选其孔径为 50~1200 微米，孔隙率为 80~98%。

本发明中，发泡金属载体的孔径大小对吸附催化剂的性能影响极大。孔径太小时，活性物质集中在载体表面，载体内部填不进去，而且气体流动性降低。孔径太大时，比表面积降低，活性物质利用率低。孔径的均匀性越好，孔内活性物质分布越好，其利用率均衡，且充分发挥作用，尾气净化的效率会越好。经试验，发泡金属作为催化转化器载体孔径选为 50~1200 微米时，效果较好，当孔径为 400~800 微米时为最优。

本发明中，当发泡金属载体孔隙率 80~98% 时，即可用做催化转化器载体。一般来讲孔隙率越大，载体性能越好。实际应用中优选孔隙率 95~98%。

制备本发明汽车尾气催化转化器中，采用电镀方法制备孔径为 50~1200 微米，孔隙率 80~98% 的发泡金属，再经过如高温氧化、电化学阳极氧化、有机酸热腐蚀的预处理以形成表面致密的氧化薄层。这样不仅增强了与催化剂涂层组分以及催化剂涂层氧化物如氧化铝、氧化锆、氧化铈的结合力，还提高了载体材料的抗高温氧化能力，可提高催化剂的净化效率和使用寿命。

本发明汽车尾气催化转化器的制备过程中，发泡金属载体与催化剂活性组分结合的工艺包括有机酸热腐蚀、浸渍涂覆和烧结的工艺过程。这样的结合方式使得在载体表面形成多层复合氧化物膜，增强了发泡金属载体与催化剂活性组分结合的牢固性。进而使催化剂具有较好的耐热冲击和机械冲击性能，且净化效率提高，使用寿命得到延长。

采用不锈钢筒形壳体 1，减振垫 2，以上述发泡金属作为载体，以上述方法制备的催化剂作为内芯制作成汽车尾气催化转化器，具有耐热冲击和机械冲击，比表面积大，净化效率高，使用寿命长的优点。

### 【实施例 1】

(一)、发泡镍金属的制备及预处理：采用公知的电镀工艺制备厚度 1.5~3.0 毫米，孔隙率为 95~98%，孔径 400 微米的发泡镍铬合金，其孔径分布均匀，无封孔，无窗孔，具有一定的机械性能和柔软性能。其中镍铬合金电镀工艺及配方如下表 1：

表 1 电镀发泡镍合金工艺和配方

组成及工艺条件	(g/L)
CrCl <sub>3</sub> · 6H <sub>2</sub> O	50 ~ 80
NiCl <sub>2</sub> · 6H <sub>2</sub> O	20 ~ 75
甲酸 (mL/L)	10 ~ 95
H <sub>3</sub> BO <sub>3</sub>	20 ~ 50
NaBr	40 ~ 90
pH 值	1 ~ 4
温度 (℃)	20 ~ 60
Jk (A/dm <sup>2</sup> )	2 ~ 10

阳极采用惰性石墨电极，阴极采用导电发泡塑料。同时，为了改善镀层的质量还添加了少量添加剂，如十二烷基磺酸钠和香豆素，镀层金属镍含量在 60 ~ 90%，铬含量 10 ~ 40%。

电镀法制备的发泡镍铬合金，经过有机酸热腐蚀 1 ~ 5 小时后，就可以直接用作汽车尾气催化转化器载体了。

(二)、汽车尾气催化转化器的制备：催化剂涂层含有纳米  $\gamma$ -氧化铝和纳米氧化锆的混和组分（其中氧化铝和氧化锆的比例为 0: 3 ~ 3: 0）。把一定比例的氧化铝和氧化锆混合物粉末浸渍到温度为 30 ~ 80℃，含有铈盐的饱和溶液中形成乳状液，浸渍时间控制在 2 ~ 5 个小时。然后在该温度下，将该乳状液浸渍在有机酸热腐蚀过的金属合金载体上，浸渍时间为 2 ~ 4 小时，并通过压缩空气流吹掉或者离心甩掉多余的乳液。将浸渍好的金属合金载体加热到 400 ~ 600℃，并保温 1 ~ 8 小时，然后冷却至室温。

将负载过又一载体的金属合金烧结好，冷却后，用有机酸进一步热处理，然后再将其浸渍到含有可溶性铈盐、铈盐和少量镁盐的溶液中。保持温度为 30 ~ 80℃，时间 2 ~ 4 小时。然后经过与上述相同的处理过程烧结得到最终用于汽车尾气催化转化器的催化剂。

采用不锈钢筒形壳体 1，减振垫 2，以上述方法制备的催化剂卷绕或叠层后作为内芯制作成汽车尾气催化转化器。

## 【实施例 2】

(一)、发泡镍金属的制备及预处理：同实施例 1。



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(二)、汽车尾气催化转化器的制备：将经有机酸处理 1~5 小时的发泡镍铬合金，直接浸渍到含有一定比例可溶性铝盐、锆盐、铈盐、铈盐及适量其它组分的混和溶液中，去掉多余溶剂，经烘干后，加热到 400~600℃，保持 2~6 小时。冷却至室温后，再反复进行有机酸腐蚀、浸渍、烘干和烧结，在载体表面形成多层复合氧化物膜，直到达到技术要求为止。

采用不锈钢筒形壳体 1，减振垫 2，以上述方法制备的催化剂作为内芯制作成汽车尾气催化转化器。

#### 【实施例 3】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 50 微米的发泡镍铬合金，制备工艺同实施例 1。

#### 【实施例 4】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 200 微米的发泡镍铬合金，制备工艺同实施例 1。

#### 【实施例 5】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 600 微米的发泡镍铬合金，制备工艺同实施例 1。

#### 【实施例 6】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 800 微米的发泡镍铬合金，制备工艺同实施例 1。

#### 【实施例 7】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 1000 微米的发泡镍铬合金，制备工艺同实施例 1。

#### 【实施例 8】

制作汽车尾气催化转化器，其载体采用厚度 1.5~3.0 毫米，通孔率 95~98%，孔径 1200 微米的发泡镍铬合金，制备工艺同实施例 1。

将上述实施例制成的汽车尾气催化转化器，经 30000 公里的道路整车试验，其 CO、HC、NO<sub>x</sub> 的转化率（%）测试结果见下表：

实例	实施 例 1	实施 例 2	实施 例 3	实施 例 4	实施 例 5	实施 例 6	实施 例 7	实施 例 8
孔径 (微米)	400	400	50	200	600	800	1000	1200
CO 转化率 %	91	94	80	83	95	93	87	75
HC 转化率 %	94	93	75	76	93	90	83	70
NO <sub>x</sub> 转化率 %	72	70	<del>50</del>	55	<del>74</del>	73	71	60

将实施例 2、3、4、5、6、7、8 做孔径-转化率趋势曲线图，见附图 3。由图中可看到发泡镍金属作为转化器催化剂载体时，其孔径大小对整个催化转化器的性能影响很大，当孔径为 50~1200 微米时，转化效果较好，当孔径为 400~800 微米时，其转化效果最优，CO、HC 转化率可在 90%以上，NO<sub>x</sub> 转化率可在 70%以上。

# 说明书附图

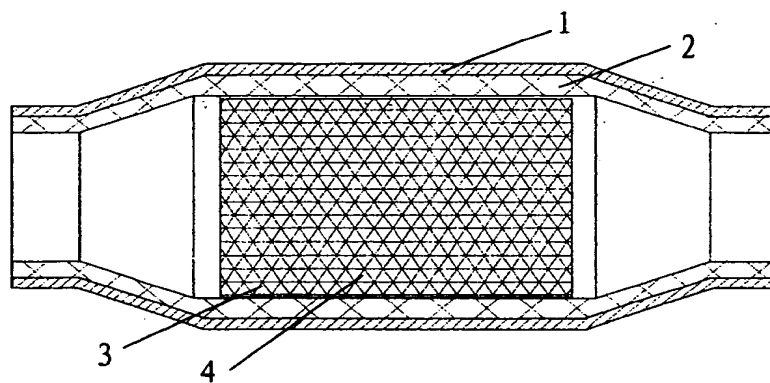


图 1



图 2

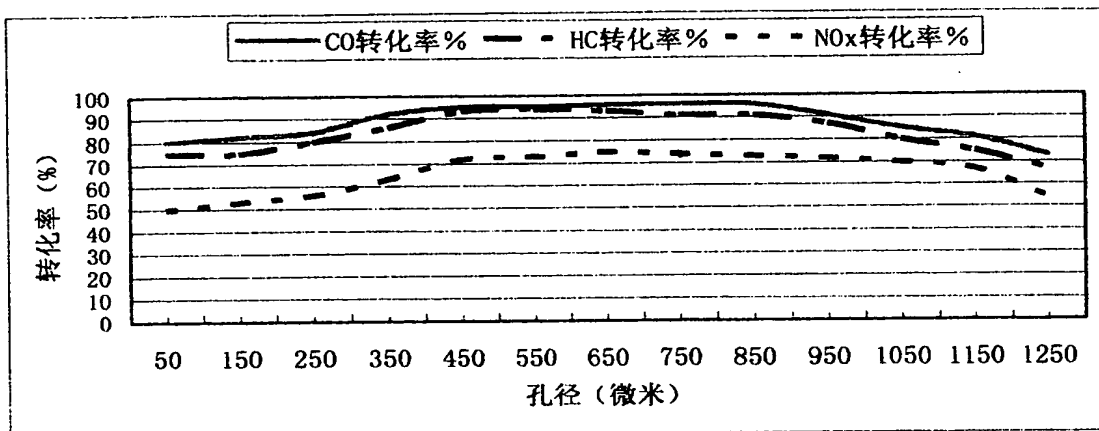


图 3

## ENGLISH TRANSLATION DOCUMENT

The following attached document is the English Translation Document for the  
below referenced Chinese patent application.

Application Date: 2003 04 30

Application Number: 03 1 14399.7

Application Type: Invention

Title: Automobile Exhaust Catalytic Converter Devices

Applicant: BYD LTD.

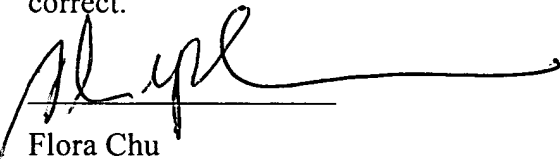
Inventors: Chuanfu Wang, Junqing Dong, Chunbo Li, Yi Liu

Attorney Docket: BYD-US2003-003

### Translation Certification

I hereby certify that the following translation of the respective certified copy is

correct.

A handwritten signature in black ink, appearing to read 'Flora Chu', is written over a horizontal line.

Flora Chu

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## Abstract of Invention

This invention relates to a type of automobile exhaust catalytic converter, including substrate, vibration reduction layer, metal substrate, and catalyst coating. The metal substrate is made of porous metal with pore diameter between 50 to 1200  $\mu\text{m}$  and the pore density  
5 between 80 to 98%. The coating layer of catalyst ingredient is securely attached to the porous metal substrate by etching it with heated organic acid, immersing, and calcining. Said automobile exhaust catalytic converter device is resistant to heat and mechanical impact, has high rate of purification and long useable lifespan.

## Automobile Exhaust Catalytic Converter Devices

### Field of Invention

This invention relates to a type of automobile exhaust catalytic converter device. Particularly, it related to the substrate for said catalyst.

### 5 Background of Invention

In the system for the purification of automobile exhaust, the catalyst is the critical component of the catalytic conversion. Ceramic and metal are the materials used for the substrate. When compared with metal substrates, the disadvantages of the generally used honeycombed ceramic substrates include: they generally operate at lower temperatures  
10 (soften at 1400°C); their walls are thicker, they preheat slower, and their exhaust pressure is higher. As such, many countries are conducting research on metal substrates. The wall of a metal substrate is only  $\frac{1}{4}$  as thick as that of the ceramic substrate wall. Therefore, exhaust pressure can be lowered and the substrate for the catalyst can also be made smaller. Metal substrates have a small heat capacity and as such it can be preheated efficiently. Therefore  
15 metal substrates have the advantage that the catalyst can be electrically preheated to realize the implementation of the zero emission policy for hydrocarbons. It also has the advantage of adapting well to temperature changes.

Existing metal substrates for the automobile exhaust catalytic converter mainly use combinations of various structures of corrugated metal. Their resistance to heat and  
20 mechanical impact are lower. Their anti-oxidation ability is insufficient, especially at high temperatures, thereby affecting the automobile exhaust catalytic purifier's useable lifespan. In addition, comparatively, the specific surface area of this type of corrugated metal substrate is limited and their capability for the active ingredient of the catalyst to be adsorbed is

insufficient, thus limiting the capability to further improve the efficiency of purification for the automobile exhaust catalytic converter.

### Description of Invention

5           The object of this invention is to provide a type of automobile exhaust catalytic converter device that is resistant to heat and mechanical impact, with high purification efficiency, long useable lifespan.

          A type of automobile exhaust catalytic converter device, including shell, cushioning layer, metal substrate with catalyst coating wherein the material for said metal substrate is  
10   porous metal with pore diameter between 50 and 1200  $\mu\text{m}$  and pore density between 80 to 98%. The diameter of the above-described pore is the average diameter. It is calculated by taking a length of a section of the porous material and divide by the number of radially joined pores that are connected in that length. The pore density is, in percentage, the volume of the pores as compared to the volume of the metal in its natural condition.

15           A further description of said material for the porous metal is that it includes two components (A and B) of metal or metal alloys.

          The A component is nickel and is 60 wt.% to 100 wt.% of the porous metal material.

          The B component is 0 wt.% to 40 wt.% of the porous metal material and contains one of more of the following metals: chromium, Cr aluminum, Al, iron, Fe, cobalt, Co  
20   molybdenum, Mo, zinc, Zn, zirconium, Zr, vanadium, V, titanium, Ti, cerium, Ce, lanthanum, La, and neodymium, Nu.

          A better specification of said porous metal material is that the pore diameter is between 400 $\mu\text{m}$  and 800 $\mu\text{m}$  and its pore density is between 95% and 98%.



The composition of the catalyst coating includes metal elements, rare earth metals and small quantities of precious metals. The metal elements include one or more of the following: calcium, Ca, barium, Ba, magnesium, Mg, zirconium, Zr, zinc, Zn, and aluminum, Al. The rare earth metals include one or more of the following: cerium, Ce, lanthanum, La, praseodymium, Pr, and neodymium, Nu. The precious metals include one or more of the following: palladium, Pb, platinum, Pt, rhodium, Rh, and ruthenium, Ru.

One or more of the following can also be added as a component for said catalyst coating:  $\gamma$  oxides of aluminum, oxides of zirconium, and oxides of cerium.

Said porous metal material is fabricated using electroplating.

The surfaces of the walls of the pores of said porous metal material have a compact oxide layer.

The advantages of the automobile exhaust catalytic converter device of this invention are: resistant to heat and mechanical impact, large specific surface area, high purification efficiency, strong adhesion between substrate and catalyst coating, and long useable lifespan

The following refers to attached figures showing embodiments to explain this invention in further detail.

#### Description of Attached Figures

Figure 1 is the diagram of a cross section of an embodiment of the automobile exhaust catalytic converter device of this invention.

Figure 2 shows the enlarged structure picture of the pores of the material for the substrate of an embodiment of the automobile exhaust catalytic converter device of this invention

Figure 3 is a graph of catalytic conversion rate as a function of the pore diameters of the metal substrate for embodiments of the automobile exhaust catalytic converter device of this invention.

## 5 Methods of Implementation

Please refer to Figure 1. This invention provides an automobile catalytic converter device, including the shell (1), the cushioning layer inside the shell (2), the metal substrate (3) and the catalyst coating (4) is coated onto the metal substrate. The metal substrate is made from porous metal with its average pore diameter between 50 to 1200 $\mu$ m and the pore  
10 density between 80 to 98%.

Figure 2 is the micrograph showing the structure of the pores of them material for the metal substrate of the automobile exhaust catalytic converter device of this invention made with JEOL Company's JSM-5610. The micrograph clearly shows that the porous metal has a 3 dimensional net structure, with its skeletal structure adjoining each other and its pores  
15 connected. The porous metal has a higher pore density and structural strength. The preferred specifications for the material of the substrate for the automobile exhaust catalytic converter device of this invention are between 50 and 1200 $\mu$ m for the pore diameter and between 80 and 90% the pore density is and the substrate for the automobile exhaust catalytic converter devices.

20 In this invention, the size of the pore diameter of the porous metal substrate greatly affects the property of the adsorbed catalyst. If the pore diameter is too small, the active material concentrates on the surface of the substrate and cannot enter the inside of the substrate. Moreover, the air flow is lowered. If the pore diameter is too big, the specific

surface area is lowered and the utilization rate of the active material is low. The more uniform the spread of pore diameter, the more evenly distributed are the active ingredient material inside the pores and the more evenly are the utilization rate of the active ingredient materials thus allowing it to be fully utilized, and the efficiency of the exhaust purifier is better. After testing, the results are better when the pore diameter of the porous metal for the substrate of the catalytic converter device is between 50 and 1200 $\mu$ m. The results are the best when the pore diameter is between 400 and 800 $\mu$ m.

In this invention, when the pore density of the porous metal substrate is between 80 and 98%, then it can be used as the substrate for the catalytic converter device. Usually, the larger the pore density, the better the properties of the substrate. However, in practical applications, the best specification for the pore density is between 95% and 98%.

In the fabrication of the automobile exhaust catalytic converter device of this invention, electroplating is used to fabricate the porous metal with pore diameter of between 50 and 1200 $\mu$ m and pore density of between 90 to 98%. Processes such as high temperature oxidation, electrochemical cathode oxidation, and etching with heated organic acid as pre-treatment are used to form the thin dense oxide layer on the surface. This not only strengthens the adhesion between the catalyst coating layer and the oxidized catalyst costing layer such as oxides of aluminum, zirconium and cerium, it also increases the ability of the substrate material to resist high temperature oxidation and can increase the purification efficiency and the useable lifespan of the catalyst.

In the process to fabricate the automobile exhaust catalytic converter device of this invention, the technology of the adhesion between the porous metal substrate and the active ingredient of the catalyst includes: etching with heated organic acid, immersion to coat, and

calcination. This type of adhesion method allows multi-layers of membranes of oxidized compound to form on the surface of the substrate, strengthening the adhesion between the porous metal substrate and the active ingredient of the catalyst. This enables the catalyst to have better resistance to heat and mechanical impact, increases the purification rate, and  
5 lengthens the useable lifespan.

The automobile exhaust catalytic converter device is fabricated using stainless steel shell (1), vibration reduction cushion (2), above described porous metal as substrate and above described fabrication method for the catalyst to form its core. It has the following advantages: it is resistant to heat and mechanical impact, it has a large specific surface area,  
10 high purification efficiency and long useable life span.

#### Embodiment 1

(1) The pre-treatment and fabrication of porous nickel metal: Use publicly known electroplating technology to fabricate thickness of between 1.5 to 3.0 mm, pore density of between 95 to 98%, pore diameter of 400 $\mu$ m of porous nickel chromium alloy its pore  
15 diameter uniformly distributed, with no orifices or windowless pores, having a predetermined mechanical property and flexibility. The technology and specification for the nickel chromium alloy electroplating are listed in Table 1.

Table 1 The Technology and Formula for the Electroplating of the Porous Nickel Alloy

Composition and Technology Conditions	( g/L )
CrCl <sub>3</sub> ·6H <sub>2</sub> O	50 ~ 80

NiCl <sub>2</sub> ·6H <sub>2</sub> O	20 ~ 75
Formic Acid ( mL/L )	10 ~ 95
H <sub>3</sub> BO <sub>3</sub>	20 ~ 50
NaBr	40 ~ 90
PH level	1 ~ 4
Temperature ( °C )	20 ~ 60
Current Density (Jk)A/dm <sup>2</sup> )	2 ~ 10

The positive electrode uses an inert graphite electrode. The negative electrode uses a conducting porous sponge-like material. A small quantity of additive, such as dodecyl sodium dodecyl sulphonate and coumarin is added to improve the material quality of the plating layer. The plated metal contains 70 to 90% nickel and 10 to 40% chromium.

After the porous nickel chromium alloy that is fabricated by electroplating is etched with heated organic acid for 1 to 5 hours, it can then be used directly as the substrate for the automobile exhaust catalytic converter device.

(2) The fabrication of the automobile exhaust catalytic converter device: The composition of the catalyst coating layer contains a mixture of nanometer alumina and nanometer zirconia, where the ratio of the nanometer alumina and nanometer zirconia is between 0:3 and 3:0. Immerse a pre-determined ratio of the mixture of the powdered

nanometer alumina and nanometer zirconia in a mixture of a saturated solution of cerium salt at a temperature of 30 to 80°C for about 2 to 5 hours to form a slurry. At that temperature, immerse the porous metal substrate that has already been etched with heat in organic acid in said slurry for 2 to 4 hours. Then, blow pressurized air or use a centrifuge to  
5 remove the excess suspension from the substrate. The porous metal substrate that has been immersed with the emulsion liquid is heated at 400 to 600°C for 1 to 8 hours. It is then cooled to room temperature.

After cooling the porous metal alloy substrate that has been calcined, it is further heat treated in organic acid, and then immersed in a solution containing soluble cerium salt,  
10 rhodium salt and small amounts of manganese salt at a temperature of 30 to 80°C for 2 to 4 hours. The catalyst for the automobile exhaust catalytic converter device is finally obtained after the it has been calcined again as described above.

The automobile exhaust catalytic converter device is made with a cylindrical shaped stainless steel shell (1), cushioning padding (2), and the inner core formed by the catalyst  
15 fabricated using above said method and after being laminated or coiled.

## Embodiment 2

(1) The pre-treatment and fabrication of porous nickel metal: same as Embodiment 1.

(2) Fabrication of automobile exhaust catalytic converter: Directly immerse the porous nickel chromium alloy that has been treated with organic acid for 1 to 5 hours in a solution  
20 mixture containing a predetermined ration of soluble aluminum salt, zirconium salt, cerium salt rhodium salt and an suitable amount of other ingredients. Remove excess solvent, then heat dry. Increase the temperature to 400 to 600°C and hold the temperature for 2 to 6 hours. Cool to room temperature then repeat etching with organic acid, immersion, heat dry and

calcinations processes multiple times to form multi-layers of oxidized compound membrane on the surface of the substrate until the desired technology result is obtained.

The automobile exhaust catalytic converter device is made with a cylindrical shaped stainless steel shell (1), vibration reduction cushioning (2), and the inner core formed by the catalyst fabricated using above said method.

#### Embodiment 3

To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 50 $\mu$ m.

#### 10 Embodiment 4

To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 200 $\mu$ m.

#### Embodiment 5

15 To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 600 $\mu$ m.

#### Embodiment 6

20 To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 800 $\mu$ m.

### Embodiment 7

To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 1000 $\mu$ m.

### 5 Embodiment 8

To fabricate the automobile exhaust catalytic converter device, the fabrication technique is the same as Embodiment 1 where the substrate is a nickel chromium alloy with a thickness of 1.5 to 3.0mm; its pore density is 95 to 98%, and its pore diameter is 1200 $\mu$ m.

10 The results for the conversion rates for CO, HC, NO<sub>x</sub> after test driving for 30,000 km the above-stated embodiments of the automobile exhaust catalytic converter device of this invention are listed in the following table.

Embo- diment	Embo- diment 1	Embo- diment 2	Embo- diment 3	Embo- diment 4	Embo- iment 5	Embo- Diment 6	Embo- Diment 7	Embo- Diment 8
Pore diameter ( $\mu$ m)	400	400	50	200	600	800	1000	1200
CO conversion rate %	91	94	80	83	95	93	87	75
HC conversion rate □	94	93	75	76	93	90	83	70
Nox conversion rate □	72	70	50	55	74	73	71	60



Figure 3 shows the graph of the relationship between the pore diameter and the conversion rates for Embodiments 2, 3, 4, 5, 6, 7, and 8. The figure shows that when porous nickel is used for the substrate for the catalyst, the size of the pores greatly affects the effectiveness of the catalytic converter device. When the pore diameter is between 50 to 1200 $\mu\text{m}$ , the conversion rate is comparatively good. The conversion rate is the best when pore diameter is 400 to 800 $\mu\text{m}$  where the CO and HC conversion rate above 90% and the NO<sub>x</sub> rate above 70%.

## Claims

1. A type of automobile exhaust catalytic converter, including shell, vibration reduction layer, metal substrate with catalyst coating. Its characteristics are: the material for said metal substrate is porous metal with pore diameter between 50 $\mu$ m and 1200  $\mu$ m and pore density  
5 between 80 to 98%.

2. Said automobile exhaust catalytic converter of claim 1, its characteristics are: said material for the porous metal includes two components (A and B) of metal or metal alloys.

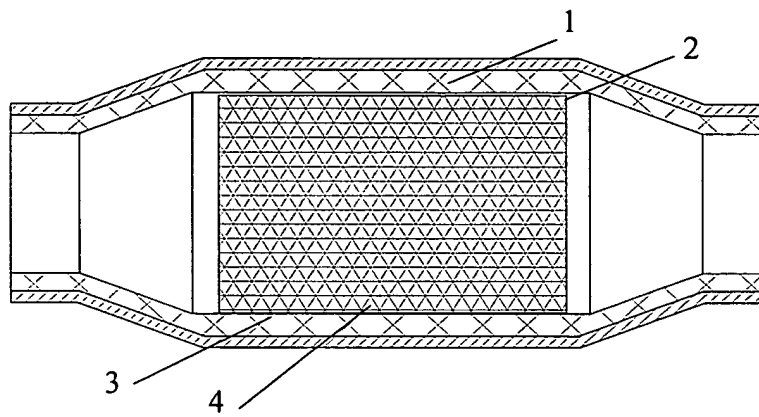
The A component is nickel and is 60 wt.% to 100 wt.% of the porous metal material.

The B component is 0 wt.% to 40 wt.% of the porous metal material and contains one  
10 of more of the following metals: chromium, Cr aluminum, Al, iron, Fe, cobalt, Co molybdenum, Mo, zinc, Zn, zirconium, Zr, vanadium, V, titanium, Ti, cerium, Ce, lanthanum, La, and neodymium, Nu.

3, Said automobile exhaust catalytic converter of claim 1 or 2, its characteristics are: the pore diameter of said porous metal is between 400 $\mu$ m and 800 $\mu$ m and its pore density is  
15 between 95% and 98%.

4. Said automobile exhaust catalytic converter of claim 1, its characteristics are: the composition of the catalyst coating includes metal elements, rare earth metals and small quantities of precious metals. The metal elements include one or more of the following: calcium, Ca, barium, Ba, magnesium, Mg, zirconium, Zr, zinc, Zn, and aluminum, Al. The  
20 rare earth metals include one or more of the following: cerium, Ce, lanthanum, La, praseodymium, Pr, and neodymium, Nu. The precious metals include one or more of the following: palladium, Pb, platinum, Pt, rhodium, Rh, and ruthenium, Ru.

5. Said automobile exhaust catalytic converter of claim 4, its characteristics are: one of more of the following can also be added as a component for said catalyst coating:  $\gamma$  alumina, zirconia, and oxides of cerium.
6. Said automobile exhaust catalytic converter of claim 1, its characteristics are: said  
5 porous metal material is fabricated using electroplating.
7. Said automobile exhaust catalytic converter of claim 1, its characteristics are: the surfaces of the walls of the pores of said porous metal material have a dense oxide layer.
8. Said automobile exhaust catalytic converter of claim 7, its characteristics are: the  
10 oxide layer on the surfaces of the walls of the pores of said porous metal material is formed by high temperature oxidation or electrochemical positive electrode oxidation or etching with heated organic acid.



5

Figure 1



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Figure 2

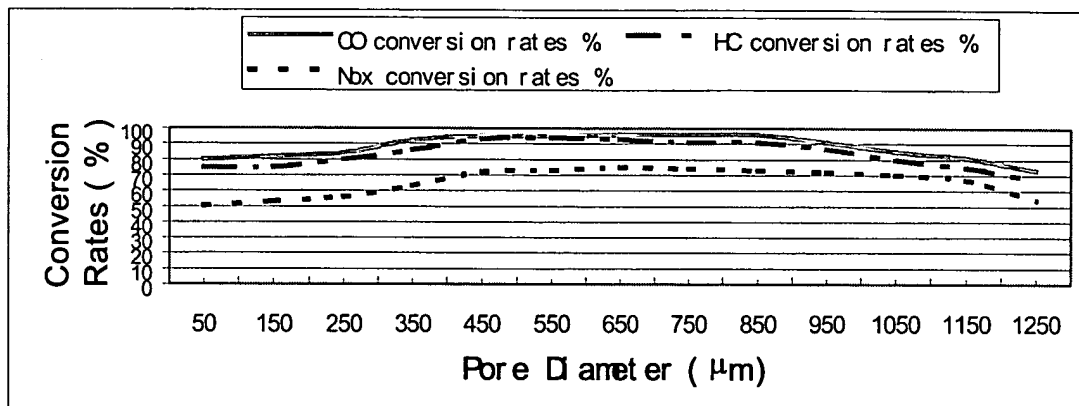


Figure 3